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Published in:
Proceedings of EuroCorr 2014

Publication date:
2014

[Link back to DTU Orbit](#)

Citation (APA):
Piotrowska, K., Conseil, H., Jellesen, M. S., & Ambat, R. (2014). Corrosion reliability of electronics: the influence of solder temperature on the decomposition of flux activators. In *Proceedings of EuroCorr 2014*

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Corrosion reliability of electronics: the influence of solder temperature on the decomposition of flux activators

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Summary

This manuscript gives a brief overview on the studies of thermal decomposition of solder flux systems commonly used in the electronic industry. Changes in chemical composition and structural changes of the flux components have been investigated as a function of temperature. Six weak organic acids, serving as flux activators, have been studied. Additionally, eleven industrially used solder flux systems have been investigated towards their thermal decomposition pattern. The results show the formation of additional species at high soldering temperatures, some having more aggressive nature than the initial flux components.

1 Introduction

The manufacturing process of printed circuit board assemblies (PCBAs) requires a careful choice of soldering materials as well as those supporting the soldering process, such as no-clean flux systems. The reliability of solder joints is influenced not only by the method of soldering, solder material itself or possible after-cleaning process, but also by the flux properties and its reactions with the components of the assembly [1]. The solderability properties of the metals can be significantly improved by the use of flux systems. They clean the joining components from contaminating films and oxides, protect the cleaned surface from reoxidation until the coating metal or solder melts and then, by reacting with it, allow the solder to adhere to a corrosion-free material, making a mechanically robust joint [1, 2]. With the introduction of no-clean flux systems for the automated (wave, reflow or selective) soldering, tiny levels of process related residues were distributed all over the surface of the assembly. Although the residues were expected to be benign, in practise the chemical nature and behaviour of solder flux systems are significant concern to the long-term stability and reliability of the components in electronic devices. At the soldering temperatures, any thermal degradation/transition products of the flux must be either non-corrosive, or else it must be possible to remove them completely [2]. Typically, the commonly used flux systems consist of: **activators** (organic acids, halide compounds or combination

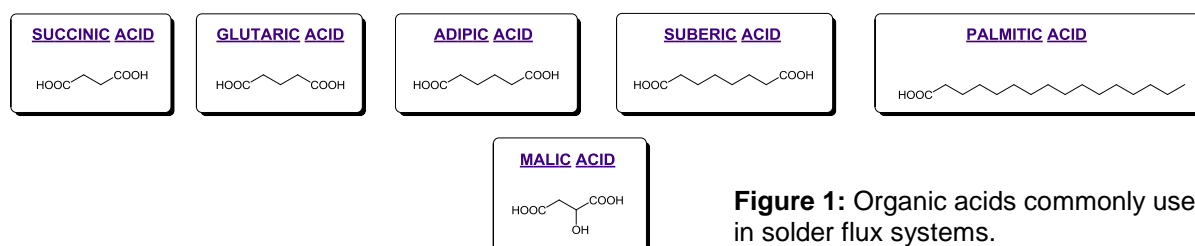


Figure 1: Organic acids commonly used in solder flux systems.

of both), **solvents** (alcohols, ethers, hydrocarbons, water etc.), **vehicles/binders** (solids, non-volatile liquids or combination of both) and **additives** (surfactants, stabilizers, inhibitors, dyes, plasticizers etc.) [3, 4]. Some of the weak organic acids (WOAs), serving as activators, are shown in Figure 1.

In humid environment water from the surrounding air is attracted by such residues and dissolves them. When this occurs, ions can carry electrical current and enter into chemical reactions like corrosion [5-11]. All above mentioned acids differ in their solubility in water (malic and glutaric – the best soluble), but they have more or less similar pK_a values (around 3.4-5.4). This value reflects the ability of the acid to be ionized in the solution (its strength). Acid strength is inversely proportional to the pK_a value. Among the mentioned WOAs, malic acid has the lowest pK_a value. This is due to its slightly different chemical nature as illustrated in Figure 2.

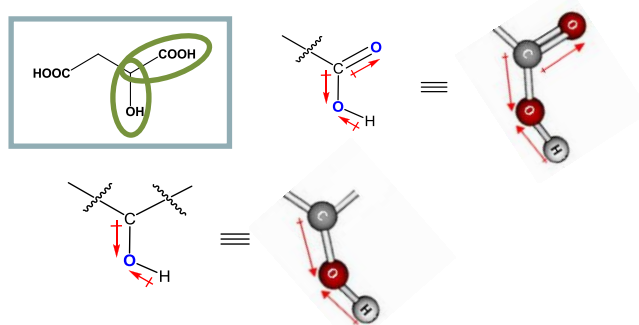


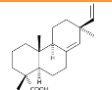
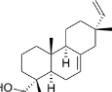
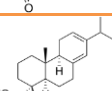
Figure 2: Polarizability of functional groups in malic acid.

The additional hydroxyl group in malic acid's structure has high affinity to water molecules. Hence, having this WOA in the flux system used for soldering and the residue left after that process can be found to have higher affinity towards humidity and therefore higher influence on climatic reliability [12].

As for the acids used as activators, there are also acids coming from the rosin vehicle used in the solder flux. In contrast to the resin being a polymeric hydrocarbon material with a terpene-derivative based core, rosin is not a polymer but a mixture of about 8 structurally closely related acids (isomers) (Table 1). Depending on various factors, the ratio between the isomers can differ, hence giving different physical properties of the rosin.

Table 1: Properties of rosin acids.

Name	Structure	Molecular formula and Molar mass	Melting point	Boiling point	pK_a
ABIETIC ACID		$C_{20}H_{30}O_2$ 302.45 g/mol	140°C / 173°C	439.5°C	6.4-7.15
NEOABIETIC ACID		$C_{20}H_{30}O_2$ 302.45 g/mol	-	433.4°C	6.59
PALUSTRIC ACID		$C_{20}H_{30}O_2$ 302.45 g/mol	162-167°C	440.25°C	7.27
DEHYDRO-ABIETIC ACID		$C_{20}H_{28}O_2$ 300.44 g/mol	172-176°C	425.1°C	5.7-7.25, 6.52

PIMARIC ACID		$C_{20}H_{30}O_2$ 302.45 g/mol	217- 218°C	413.2°C	6.45
ISOPIMARIC ACID		$C_{20}H_{30}O_2$ 302.45 g/mol	-	-	6.44
LEVOPIMARIC ACID		$C_{20}H_{30}O_2$ 302.45 g/mol	150°C	-	6.46

The aim of presented work is to investigate the decomposition pattern of the activators commonly used in solder flux systems. The changes in the activators' structures have been studied in terms of temperature and time of exposure to high temperatures simulating the top and bottom of PCB surfaces during the soldering process.

2 Materials and analysing methods

2.1 Materials

Six weak organic acids serving as activators in the commonly used solder flux systems [2, 9, 13-15] have been examined in terms of their decomposition patterns and possible decomposed species formation. The activators studied are: **DL-malic acid, succinic acid, glutaric acid, adipic acid, suberic acid** and **palmitic acid**.

Additionally, the rosin acid used in commercial flux system has been analyzed for its behavior in a simulated soldering temperature profile. All the acids have been diluted in isopropyl alcohol to obtain 5% w/v solutions, simulating the average WOA content in solder fluxes.

Eleven commercial no-clean flux systems are studied to understand the effect of acid type and acid value in comparison with the studies conducted using pure WOAs. Table 2 gives the information about the type of acid and its number in the chosen tested commercial flux systems. All of them are liquid-type flux used for wave or selective soldering process.

Table 2: Flux systems and their characteristics.

Flux symbol	Activator	Acid value [mg KOH/g]
SF1	Succinic acid	18.7
SF2	Succinic + glutaric + adipic acids	31.5 ± 2.0
SF3	Succinic + resin & rosin acids	23.4
SF4	Rosin ester	15.7 – 16.5
SF5	Rosin ester	29.0 ± 2.0
SF6	Rosin ester	59.5 ± 2.0
SF7	Rosin ester	29
SF8	modified rosin acid	55.5 ± 7.8
SF9	Succinic + resin & rosin acids	19.7
SF10	Betaine salt	60.0
SF11	halides	32

2.2 Flux activation treatment

The WOAs and flux systems have been thermally activated at two temperatures, namely $170 \pm 5^\circ\text{C}$ and $250 \pm 5^\circ\text{C}$, to simulate the top and bottom part of the PCB surface during the soldering process. The residues obtained were subjected for further analysis. As a reference, the residue obtained at room temperature evaporation has been tested. In some cases an additional activation treatment at $350 \pm 5^\circ\text{C}$ has also been conducted in order to get better understanding of the decomposition behavior.

2.3 Analysing techniques

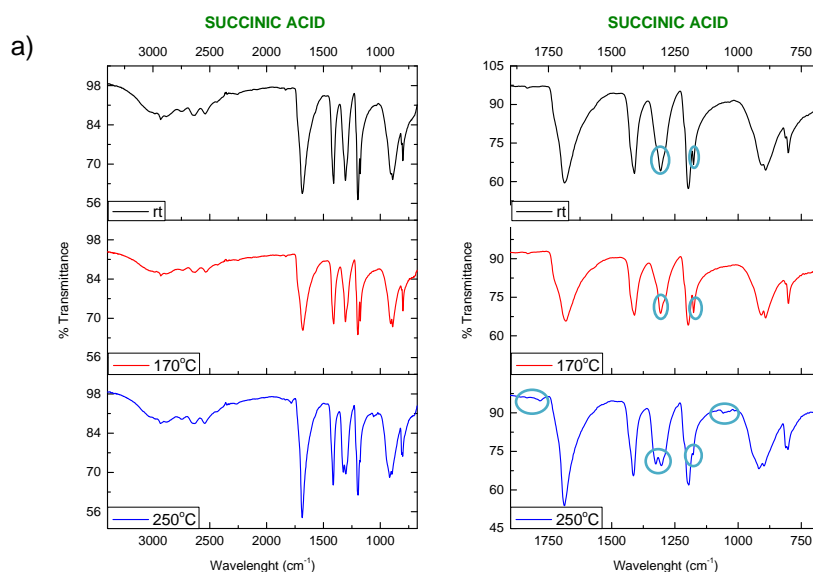
In order to observe the possible chemical structural changes of activators, Fourier Transform Infrared Spectroscopy (FT-IR) has been used. The formation of new species during the thermal treatment was obtained from the IR spectrum from the appearance of new absorption peaks. The ATR mode (Attenuated Total Reflectance) has been used for all the investigations.

For evaluation of the acid content in the sample, the standardized acid-base titration has been conducted [16]. The influence of surface area on evaporation has been investigated by conducting the experiments using the same amount of WOAs solutions and fluxes, however with different open surface areas in suitable glass vessels.

3 Results

3.1 FT-IR analysis

All six weak organic acids, commonly used as activators in the solder flux [2, 9, 13-15], have been tested in order to find their thermal decomposition products. In the case of adipic, suberic, glutaric and palmitic acids, there were no changes in the infrared spectrum even after heating up to 250°C . In the case of succinic and DL-malic acids, slight changes in the IR spectra were observed. Figure 3 shows the comparison of spectra obtained for succinic and DL-malic acids at three different temperatures. The marked peaks (see circles) in the spectra show changes after thermal treatment.



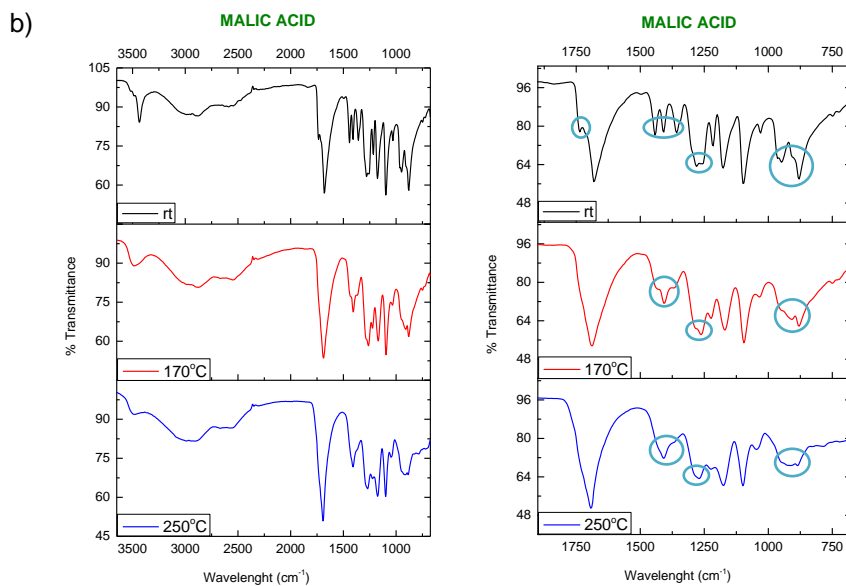


Figure 3: FT-IR spectra in the wavelength from 675 cm^{-1} to 3600 cm^{-1} to the left and with zoom of 675 cm^{-1} to 1900 cm^{-1} to the right. a) succinic acid, b) malic acid; room temperature, 170 and 250°C .

All the spectra show absorption peaks at around $2950\text{--}2870\text{ cm}^{-1}$ which are assigned to the symmetric and asymmetric CH_3 and CH_2 stretching vibration bands coming from single bonds in the organic acid chain. Changes in the succinic acid spectrum were observed at vibrational frequencies of 1785 cm^{-1} , 1325 cm^{-1} , 1303 cm^{-1} , 1179 cm^{-1} and 1062 cm^{-1} . For DL-malic acid there are more changes noticed. Comparing the spectrum measured at room temperature, the one at 250°C lacks few peaks at 1737 cm^{-1} , 1443 cm^{-1} , 1408 cm^{-1} . The absorption peaks in the region of $1300\text{--}1173\text{ cm}^{-1}$ in all the measured spectra show some distinct changes in the shapes of the peaks. In the case of DL-malic acid, the fingerprint region between $1500\text{--}500\text{ cm}^{-1}$ (a specific region for each molecule) shows in general the different pattern for all three temperatures of measurement.

3.2 Acid value determination

Figure 4 shows the values of acid number (acid content) obtained by titration of different weak organic acids and rosin acid with KOH solution. The acid number is represented as a function of the heating temperature with standard deviations given for each bar. It can be easily observed that in each case the acid values at 170°C and 250°C stay significantly high in comparison to their values at room temperature. Only at 350°C , the decrease of acid amount for some of the examined acids is clearly present (DL-malic, succinic, glutaric, and adipic). Figure 5 shows the acid values changing with the increasing temperature which illustrates the values in more detail than presented in Figure 4. The boiling point for each particular acid has been indicated. To evaluate the influence of heating time on the total evaporation of the acids, samples of solder fluxes based on succinic acid (SF1), mixture of succinic, glutaric and adipic acids (SF2), and a mixture of succinic and rosin/resin acids (SF3) have been heated up to 170°C and 250°C (Figure 6). In this measurement, the changing factor was not only the type of activator, but also the time which was prolonged up to 10 minutes. The significant loss of acid amount at 250°C can be observed in each case when the time of sample heating was longer. When heating the samples up to 170°C ,

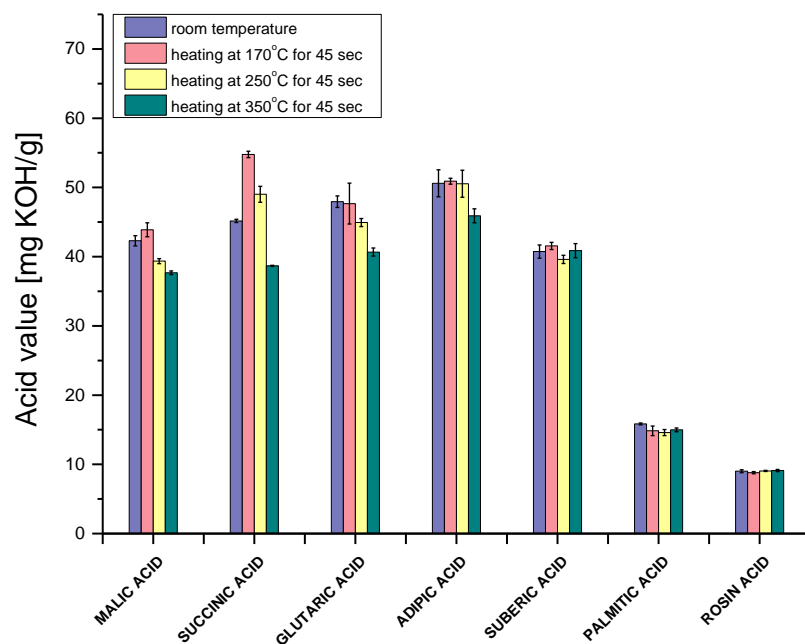


Figure 4: Acid values for six different weak organic acids and rosin acid. Error bar represents the standard deviation values for 3 repetitions.

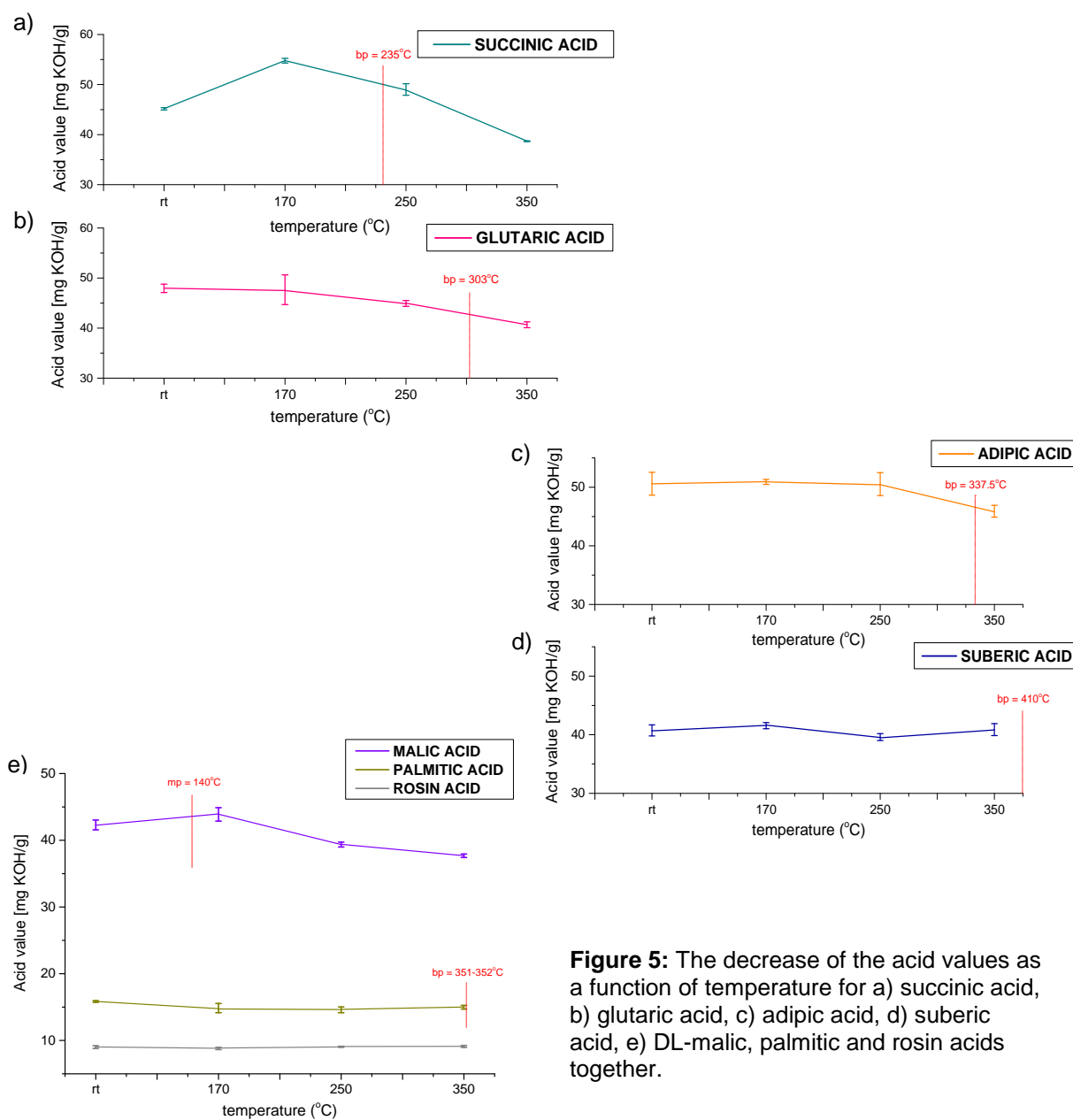


Figure 5: The decrease of the acid values as a function of temperature for a) succinic acid, b) glutaric acid, c) adipic acid, d) suberic acid, e) DL-malic, palmitic and rosin acids together.

the decrease of acid content was lower. To evaluate the behavior pattern of differently modified rosin acid activators, betaine- and halide-based fluxes at high temperatures, the same type of acid-base titration of commercially available flux systems has been conducted (Figure 7). For all flux systems SF4 – SF9, the acid content remains the same or even slightly increases. This takes place not only after heating to 170°C, but also after heating to temperatures 250°C and 350°C. In the case of betaine salt-based flux system (SF10) the acidic specimen in the sample remains on similar level at 170 and 250°C, decreasing when the temperature reaches 350°C. For flux system SF11, halide-based of rosin type, the increase of acid value can be observed.

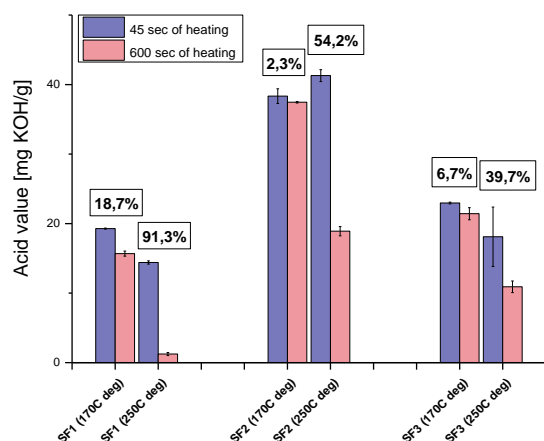


Figure 6: The decrease of acid content in different flux samples as a function of heating time and temperature.

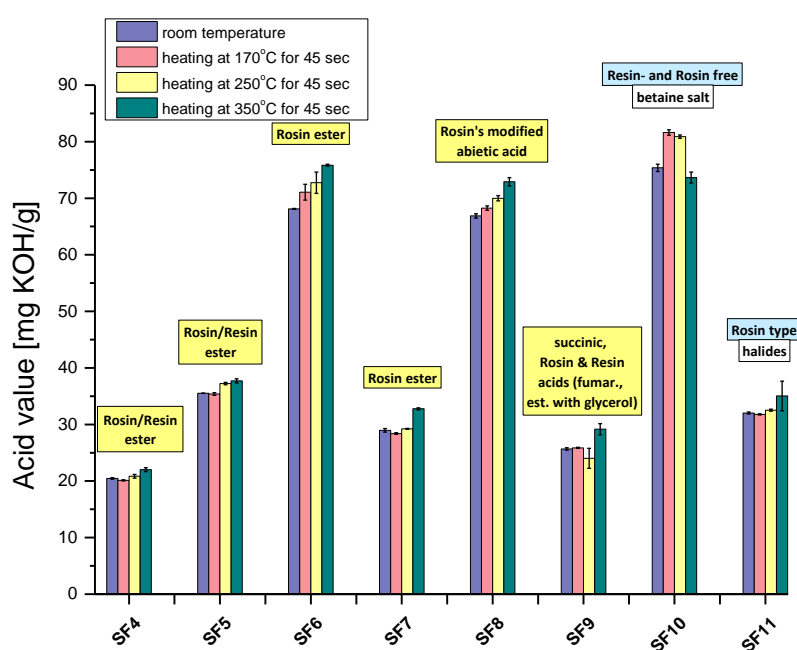


Figure 7: Changes of acid number in the fluxes containing modified rosin acids and betaine salts.

4 Discussion

4.1 FT-IR analysis

Investigation of chemical structure changes as a function of increased temperature in the case of adipic, suberic, glutaric and palmitic acids did not show any changes. Their boiling temperatures are over 300°C indicating that evaporation is not likely to take place at room temperature. However, in the case of succinic and malic acids, spectra looked different at various temperatures. Those changes can indicate the

possible partial formation of other specimens, ester-like by-products – organic acids anhydrides. At such high temperatures, simulating soldering temperatures, the evaporation of water will take place. Depending on the time of heating up the samples, the loss of water content can differ. Dicarboxylic acids may undergo decomposition in several ways - sometimes very complex - when exposed to high temperatures [5]. Everything depends on their melting and boiling points and chemical nature [15]. The simplest transformations are decarboxylation (CO_2 molecule is released from acid) and dehydration (water molecule goes away). In case of malic acid, the water molecule is formed from hydroxyl group and hydrogen atom of the nearest CH_2 group, which results in obtaining the species with double bonds (in the first step of dehydration – maleic acid, in the second one – maleic anhydride) (Figure 8b). All dicarboxylic acids may form anhydrides at their specific temperatures. This is probably the most dangerous and aggressive way of decomposition due to anhydrides' chemical nature: the ring is strained which makes anhydrides more reactive. Additional occurrence of double bonds only intensifies this property. Once they are formed, they may easily react with copper oxides [2, 15].

For succinic acid the formation of anhydride takes place at 235°C [13]. Changes in IR spectra observed around 1300 cm^{-1} can indicate the C-O bond formation for cyclic acid anhydrides ($1300\text{-}1176\text{ cm}^{-1}$). The growing peak at around 1785 cm^{-1} can be assigned to C=O vibrations in 5-unit ring (which succinic anhydride is) ($1870\text{-}1818$; $1800\text{-}1750\text{ cm}^{-1}$) [17]. Such changes can mean the existence of both succinic acid and anhydride in the measured sample (Figure 8a).

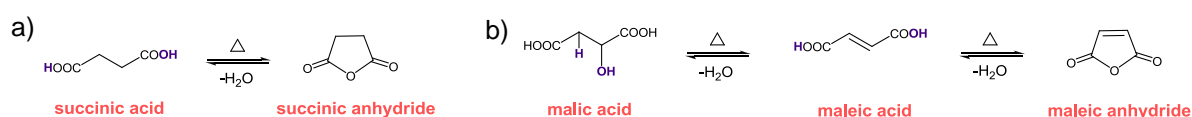


Figure 8: Decomposition products of a) succinic, and b) malic acids.

In the case of malic acid, more changes are observed. Malic acid does not boil, but decomposes at $130\text{-}140^\circ\text{C}$ to give CO , CO_2 , maleic acid and maleic anhydride (Figure 8b), it is hard to distinguish those species clearly. However, the decrease of peak intensity at around 3500 cm^{-1} can indicate the disappearance of hydroxyl groups from the sample. Even if double bonds (from maleic acid or anhydride) occur, they overlap onto those coming from single C-H bonds which is impossible to be distinguished.

4.2 Acid values

At soldering temperatures, when heating the acid samples for 45 seconds (Figure 4 and 5), there is still remaining acid on the surface. This can be the result of short evaporation time when the thermal energy is mostly consumed to evaporate the solvent firstly followed by the acid. The influence of different surface areas on evaporation has been tested by running the measurements with variable Petri dish sizes. These results indicate that evaporation rate has minimal dependency of Petri dish surface area. The graph presents a nice correlation between acid value change and chain length of the acid: the longer the chain is, the higher boiling temperature the acid has – hence the less of it will be evaporated.

At 350°C , for succinic, glutaric, adipic, and malic acids, there is a significant decrease of the acid amount present. This is surely due to the fact that their boiling temperatures are lower than 350°C . But even at this quite high temperature there is only par-

tial evaporation of the acid or possible transition into other specimens – some amount of acid is still found on the surface. In the case of suberic, palmitic, and rosin acids, there is always more or less the same acid amount as at room temperature measured samples. Their boiling points, 410°C, 351-351°C and more above 400°C respectively, are too high for the usual soldering temperatures to evaporate the acid from the surface.

Even with prolonged time of heating, there was always some amount of acid remaining in the measured samples (Figure 6). In the case of succinic acid-based flux SF1, the decrease of its amount drops down for about 90%. This can be due to the presence of resin as a film former in the flux which can possess modified structure also containing carboxylic acid groups. Hence, even with prolonged heating time, the acid still will be remaining. For SF3 based also on rosin and resin acids, the situation is the same.

As there are plenty of possible industrial modifications of rosin acids [5] which result in obtaining specimens of different physical properties, seven of commercially available flux systems were examined (Figure 7). All of them showed the tendency to increase the acid amount when heating up to 250°C and higher. Rosin does not evaporate or decompose rapidly at typical soldering temperatures [2].

Some examples of industrial rosin acid modifications are given in Figure 9. For example, when forming esters with abietic acid and reducing the number of –OH groups, the specimens of lower softening point can be obtained. Hydrogenation of rosin acid can improve its stability (depending on partial or full hydrogenation) and make it more compatible with many polymers, which allows for further modifications depending on desired properties of such materials. Dimerization of rosin acids increases both their softening point and stability.

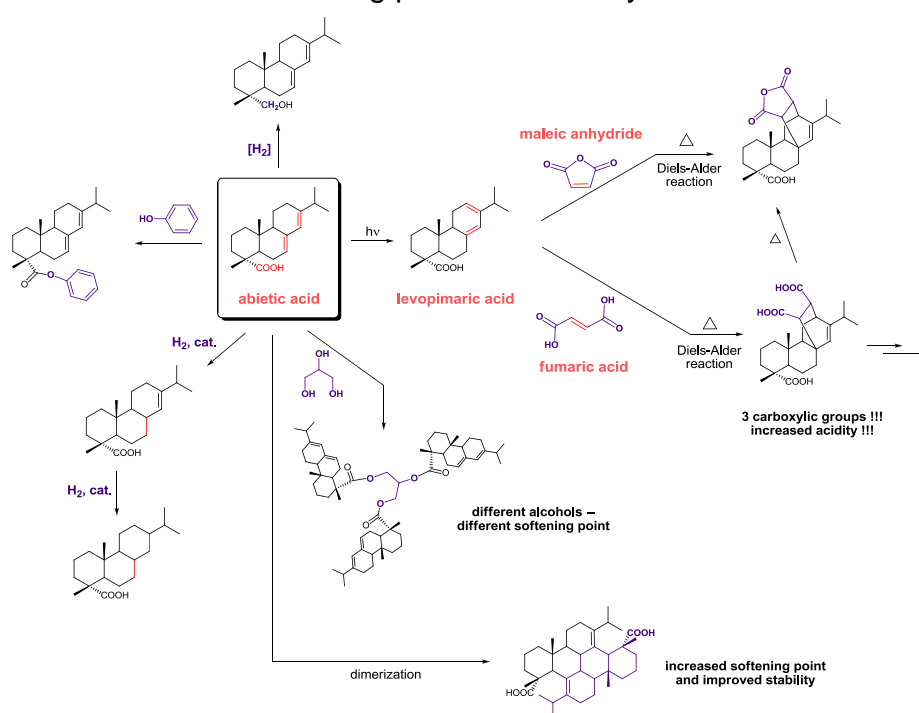


Figure 9: Some examples of industrial modifications of rosin acid.

Seen from a PCBA reliability point of view, modifications of abietic acid are a concern, since the incorporation of maleic anhydride or fumaric acid into its structure takes place. Fumaric and maleic acids are each other's isomers (fumaric – *E*, *trans*; maleic – *Z*, *cis*) which can be differentiated because of different physical and chemical properties (maleic is much stronger due to intramolecular H₂ bonding occurrence, its pK_{a1} = 1.9; for fumaric pK_{a1} = 3.0). Both of them contain double bonds in their structures which are way more reactive than single bonds present in already well

known weak organic acids. In the propitious conditions, the incorporation of either fumaric or maleic acids can easily take place (Figure 9). As a result, new types with more carboxylic groups (and hence the increased acidity) can be obtained. As such rosin acids' derivatives have high boiling temperatures, they will not easily evaporate from the PCBA surface. This makes it more possible to cause reliability problems (despite of their usually higher pK_a values).

Such modified rosin was found in the flux sample 9 (Figure 7), which contained the mixture of succinic acid and "rosin and Resin acids (fumarated, esters with glycerol)". Although the acid number of such flux is quite low, around 20, with the increase of temperature the acid content also increases. Either the new COOH groups are formed at higher temperature, or the acid molecules are released from modified rosin's acid.

The simplest betaine specimens start to decompose (or boil) at 300°C, and therefore the SF10 flux sample shows decrease in acid content although the amount of remaining acid is still significantly high.

For halide-based rosin type there can be halide ions possibly released from the structure of modified rosin's acid, which increases the acid value at higher temperatures of sample treatment.

5 Conclusions

From the reliability point of view, thermal activation of WOAs and flux systems influences their chemical decomposition pattern. This work shows that:

- Among all the tested WOAs, the succinic and malic acids undergo thermal degradation at high soldering temperatures and form additional anhydride-like species. Some of them have more aggressive chemical nature than the initial flux activators.
- In the case of all the analyzed WOAs, the thermal treatment, even at very high temperatures, resulted in significant amount of remaining acid. Even the prolonged time of heat treatment does not allow for their full evaporation.
- For rosin/resin acid-based flux systems, the increase of heating temperature resulted in higher amount of acid than in initial flux sample. This indicates the formation of/decomposition into more acidic species with the increase of temperature.

6 Acknowledgments

The research reported here has been conducted as part of the CELCORR/CreCon consortium (www.celcorr.com). Authors would like to acknowledge the consortium partners for funding support and all the help received during the program run.

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